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RESEARCH MEMORANDUM

INVESTIGATION OF EFFECT OF FLUORIDE ON CORROSION OF
2S-0 ALUMINUM AND 347 STAINLESS STEEL IN FUMING
NITRIC ACID AT 170° F

By Charles E. Feiler and Gerald Morrell

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

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INVESTIGATION OF EFFECT OF FLUORIDE ON CORROSION OF

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SUMMARY

The effect of small additions of fluoride on the corrosion of 2S-0 aluminum and 347 stainless steel by fuming nitric acid at 170° F has been evaluated quantitatively by the determination of the weight loss of metal specimens immersed in the acid. The ratio of metal surface area to volume of acid was approximately 7.5 inch^{-1} in all cases. It was found that for acids containing no fluorides the weight loss of aluminum was approximately $1/5$ that of stainless steel. Addition of 1 percent fluoride ion to the acid reduced the weight loss of both metals to practically zero even after 26 days of exposure to the acid at 170° F. The minimum quantity of fluoride ion required to inhibit corrosion was found to be approximately 0.25 and 0.5 percent for aluminum and stainless steel, respectively, in white fuming nitric acid and 0.5 and 1 percent for aluminum and stainless steel, respectively, in red fuming nitric acid (18 percent nitrogen dioxide). These fluoride percentages were based on the total weight of acid. Provided the concentration of fluoride ion was sufficient to inhibit corrosion, the source of these ions was immaterial.

Additional information concerning the effect of fluorides on corrosion was obtained by measuring the electrode potentials of the metals against a platinum reference electrode.

INTRODUCTION

Among the storage properties of fuming nitric acid, corrosion and decomposition are of foremost concern. It has been found that decomposition of white fuming nitric acid is best inhibited by the addition of approximately 20 percent nitrogen dioxide, which lowers the peak decomposition pressure by an order of magnitude (e.g., refs. 1 and 2). The addition of nitrogen dioxide, however, does not improve the corrosive

properties of these acids which attack most metals severely. Of the commercially available metals, aluminum and stainless steel alloys are among the more resistant to corrosion, but at elevated temperatures the corrosion rate of even these alloys becomes appreciable (ref. 3). This results in contamination of the acid beyond use, even though the container may not fail.

Investigation of several additives has shown that hydrofluoric acid is an effective inhibitor of corrosion of aluminum and stainless steel alloys by fuming nitric acid (refs. 4 and 5). Other experiments have shown qualitatively that potassium fluoride dihydrate also reduces the amount of corrosion of these metals by fuming nitric acid (ref. 1).

In order to obtain additional information concerning the effectiveness of fluorides as corrosion inhibitors in fuming nitric acid, an investigation was undertaken at the NACA Lewis laboratory. The experiments were conducted at 170° F, and the corrosive attack of the acid was determined from the weight loss of 2S-0 aluminum and 347 stainless steel specimens immersed in the acid. The acid was contained in tubes of the same or similar metal as the specimen. The ratio of metal surface area to volume of acid was approximately 7.5 inch⁻¹ based only on the metal surface area, including that of the specimen, in contact with acid. The duration of the experiments was limited by deterioration of the acid, which was rapid because of the large ratio of metal surface area to acid volume used. Additional information concerning the effect of fluoride on corrosion was obtained by measuring the electrode potential of the metal against the electrode potential of a platinum reference electrode.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus consisted of aluminum and stainless steel test tubes for containing the test specimens and acid during corrosion experiments and a glass cell for measuring electrode potentials.

Test tube. - A photograph of the test-tube assembly is shown in figure 1. The tubes were 7 inches long and were constructed from 52S-0 aluminum and 347 stainless steel tubing with fittings of 17S-T aluminum and 347 stainless steel, respectively. One end of the tube was closed by fuse-welding, and the other end was flared to accommodate a flare-type fitting. The ratio of metal surface area to acid volume was approximately 7.5 inches⁻¹, based on the surface area of both the tube and specimen in contact with the acid. The volume of acid used was 30 milliliters (measured at approximately 32° F) in all cases, which was sufficient to completely cover the specimens. The loaded tubes were placed in a water bath maintained at 170° ± 2° F. In order to protect the aluminum tubes from external corrosion while in the bath, the tubes were

enclosed in glass test tubes. Before opening the tubes at the conclusion of an experiment, the acid was frozen by immersing the tubes in liquid nitrogen. The purpose of this procedure was to eliminate decomposition pressure developed during the run.

Test specimens. - The test specimens, $2\frac{1}{2}$ by $\frac{3}{8}$ by $\frac{1}{16}$ inches, were cut from 16-gage 2S-0 aluminum and 347 stainless steel sheet stock. Burrs were removed by filing and by abrading with 3/0 emery cloth. The specimens were washed with water and acetone, desiccated for 24 hours, and then weighed to the nearest tenth of a milligram. The samples were placed in tubes of similar material to minimize galvanic corrosion. At the conclusion of an experiment, the specimens were treated in the same manner and the change in weight of each specimen during the experiment was determined. The variation in initial weight among the specimens was small, and therefore the surface areas were considered to have a constant value of 2.2 square inches.

Electromotive-force cell. - A sketch of the electromotive-force cell and instrumentation is shown in figure 2. The cell was constructed of pyrex glass and incorporated a sintered glass disc of fine porosity to minimize diffusion of material between the two half-cells. Electrode potentials of the specimens were measured against a platinum reference electrode immersed in acid containing no additive and were read directly from a potentiometer to the nearest millivolt. A suitably damped mirror galvanometer was used to detect the balance point. Electrode potential measurements of a given experiment were continued for periods of not more than 8 hours.

Acids and additives. - Commercial acid as received in aluminum drums was used without further treatment. Samples were transferred to glass containers and stored at 32° F until used. The chemical analysis and density of the two acids used was as follows:

Acid	Density at 32° F, g/ml	Percent by weight			
		HNO ₃	NO ₂	H ₂ O + Nonvolatile (by difference)	Nonvolatile
RFNA	1.61	78.8	18.0	3.2	0.10
WFNA	1.54	97.0	.8	2.2	.02

The additives used were c.p. grade potassium fluoride dihydrate (KF·2H₂O) and reagent grade hydrofluoric acid (HF) solution, (50.2 percent by weight). Additives were used on a percentage-by-weight basis.

Analyses. - Acid analysis was determined by the method of Air Force Specification 14104, except that total acidity was determined by direct titration of the acid in water with NaOH solution. Nonvolatile impurities were determined by weighing the solids obtained from evaporation of the acid and from heating the residue to red heat. Fluoride was determined by the method of reference 6. The accuracy of the fluoride determination appears to be of the order ± 10 percent. Density determinations were made by use of a Westphal balance.

Pretreatment method. - In order to determine the effect of pretreatment with hydrofluoric acid, some of the specimens were prepared in the following arbitrary manner: Aluminum specimens were immersed in warm 10-percent NaOH for 10 seconds and 20-percent HNO_3 for 20 seconds, then anodized in 10-percent sulfamic acid for one minute, followed by immersion in 0.25-percent hydrofluoric acid for 30 seconds. Specimens were rinsed with water after exposure to each solution. Stainless steel specimens were pickled in 20-percent HNO_3 for approximately 1 hour, followed by immersion in 1-percent hydrofluoric acid for periods of approximately 1 hour for one set of specimens and 24 hours for another set of specimens.

RESULTS AND DISCUSSION

Comparison of RFNA and WFNA

In figure 3, the weight losses of aluminum and stainless steel at 170° F in RFNA and WFNA are shown for various periods of exposure. The data show that the weight loss of aluminum is about the same in either acid, whereas the weight loss of stainless steel is greater in WFNA than in RFNA. The data also show that the weight loss of stainless steel in either acid is five or six times that of aluminum. The leveling-off of the curves indicates that the acid is deteriorating, and this results in a decrease in the corrosive attack on the metals. Deterioration of the acid was rapid because of the large ratio of surface area to volume of the experimental conditions.

Effect of Fluoride Concentration

The effect of fluoride concentration in the acid on the weight loss of aluminum and stainless steel at 170° F in RFNA and WFNA is shown in figure 4. The duration of these experiments was 3 days. The data indicate that the addition of 0.25 percent fluoride to RFNA increases the weight loss of both aluminum and stainless steel. The minimum quantity of fluoride which will inhibit corrosion in RFNA appears to be 0.5 percent for aluminum and 1 percent for stainless steel;

with WFNA the minimum quantity of fluoride appears to be 0.25 percent for either metal. A gain in weight was observed for some of the specimens, which was apparently caused by the formation of a coating on the surface of the metal. An attempt was made to remove as much of this coating as possible by abrading the specimens with a soft rubber eraser. The weight of material removed in this manner usually was less than a milligram per specimen and was in one case about 7 milligrams. If the change in weight of a specimen was sufficient to be plotted, the weight both before and after abrasion is shown. It may be concluded from figure 4 that the inhibiting material is the fluoride ion and that its source is immaterial.

Effect of Fluoride with Time

In order to verify the results shown in figure 4, the effect of various concentrations of fluoride were studied for longer periods of time. These data are shown in figure 5 and table I. All the weight-loss data presented are averages of duplicate experiments. An indication of the reproducibility of the data is shown in figure 5 by the curves for aluminum in RFNA containing 0.2 percent fluoride and for stainless steel in RFNA containing 0.5 percent fluoride for which curves data of duplicate experiments are plotted. The data of figure 5 agree closely with those of figure 4 for corresponding time periods; however, it appears that 0.25 percent fluoride is insufficient to inhibit corrosion of stainless steel in WFNA for extended periods of time. A reversal in trend shown in figure 5 is that the weight loss of stainless steel in RFNA containing 0.5 percent fluoride is greater than it is in RFNA containing 0.2 percent fluoride. In either case, the presence of fluoride results in larger weight loss than for acid containing no fluoride.

The change in weight of aluminum and stainless steel specimens exposed for 26 days to acid containing 1 percent fluoride is shown in table I. These data show gains in weight for all combinations except one, which had a small weight loss after abrasion. The acids from these experiments showed no visual evidence of metal contamination. The acids were analyzed to determine the amount of fluoride remaining in solution at the conclusion of the experiment. These data, presented in table II, show that roughly $1/2$ to $1/3$ of the fluoride remained in solution. The quantity of fluoride remaining in solution was smaller for acid stored in aluminum than in stainless steel, which corresponds to the larger gain in weight of aluminum as shown in table I.

Effect of HF Pretreatment

The results of the experiments with pretreated specimens are shown in figure 6. From these data it appears that the pretreatment used was not a particularly effective measure for corrosion inhibition. Some

inhibition was observed for pretreated stainless steel specimens in WFNA; however, it was less than that obtained by the addition of fluoride to the acid. The time of pretreatment of stainless steel with fluoride had little effect on corrosion, similar results being obtained for both time periods investigated. Reproducibility of results was considerably less for the series of pretreat experiments than for any other experiments. The reasons for this are not known but appear to be associated with the pretreatment mechanism. It is concluded from these data that the particular pretreatment used is not as satisfactory for inhibition of corrosion as addition of fluoride to the acid.

Metallurgical Examination

Photomicrographs of the cross sections of aluminum and stainless steel specimens taken before and after exposure to RFNA for 13 days are shown in figure 7. From these it can be seen that the attack on the metal by the acid was general or uniform in nature. Photographs of original specimens and specimens which were exposed to acid with and without 1 percent fluoride for 3 days are shown in figure 8. The stainless steel specimens (fig. 8(b)), which were exposed to acid containing no fluoride, are appreciably blackened and etched, whereas those exposed to acid containing 1 percent fluoride retain much of their original appearance. The effect of corrosion on the appearance of aluminum (fig. 8(a)) is less obvious because it does not blacken on exposure.

If the specimens are exposed to acid containing 1 percent fluoride for longer periods than 3 days, an appreciable thickness of coating is formed on the metal surface. Figure 9 shows aluminum and stainless steel specimens which were exposed to acid containing 1 percent fluoride for 10 days. The color of the coating was white to bronze with aluminum and was greenish-white with stainless steel. The uniformity and degree of adherence of the coating also vary; however, no special trend was observed for these properties. The quantity of metal, if any, which was removed by the acid prior to formation of the coating is not known. An indication that the amount was small is shown by the following table in which the percent of nonvolatile material present after 3 days of exposure is compared for aluminum and stainless steel in RFNA with and without 1 percent fluoride.

Metal	Nonvolatile, percent by weight		
	Original acid	No fluoride	1 Percent fluoride (HF)
Aluminum	0.10	0.53	0.28
Stainless steel	.10	4.81	.32

The increase of metal content in acid containing 1 percent fluoride is appreciably smaller than the increase in metal content in acid without fluoride. The effect, however, is less pronounced with aluminum because its weight loss is smaller.

Electrode-Potential Measurements and a Possible Inhibition Mechanism

Representative curves obtained from electrode-potential data are shown in figure 10 for stainless steel in RFNA and WFNA. The platinum electrode was positive with respect to both stainless steel and aluminum under all conditions. On the addition of 0.25 percent fluoride to the acid in the stainless steel or aluminum half-cell, a rapid increase in potential followed by a less rapid decrease was observed. After this fluctuation the potential appeared to become more stable at a value greater than the potential prior to the addition of fluoride. Similar results were obtained when acid of the stainless steel half-cell was saturated with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Addition of the fluoride caused a portion of the residual nickel salt to dissolve. In the case of the saturated aluminum half-cell, addition of fluoride caused all of the residual aluminum salt to dissolve and no attempt was made to resaturate the solution.

If the potential of the platinum half-cell is assumed to remain constant, three possible explanations for the behavior of the potential of the cell on addition of fluoride are: the increase in cell potential is caused by an increase in either junction potential or in solution potential or a combination of increase and decrease in both these potentials. From the experimental measurements, it was not possible to determine the relative changes in the two sources of potential; however, the most likely explanation appears to be that the junction potential increases slightly because of the change in the nature of the electrolyte on addition of fluoride and that the solution potential of the metal is increased because of increased attack on the metal, that is, an increase of solution potential of the metal results because hydrofluoric acid considerably attacks these metals, especially aluminum. If the solution potential of the metal is increased, an increase in the driving force of the corrosion reaction would result. Results show that fluoride reduces corrosion; and, if fluoride increases the driving force, then it must also increase the resistance of the metal to corrosion in order to agree with the reduced rate of corrosion observed experimentally. This phenomenon probably occurs because of the formation of the coating which has been observed on metal specimens exposed to acid containing fluoride. An attempt has been made to establish the identity of the coating by both X-ray and electron diffraction techniques. It was found that no pattern could be obtained, and therefore it is concluded that the coating is amorphous in structure.

CONCLUDING REMARKS

The ratio of metal surface area to acid volume of the experimental tubes used in these experiments was approximately 7.5 inch^{-1} as compared with that of a standard 55-gallon drum which is approximately 0.25 inch^{-1} . From the extrapolation of the 26-day data shown in table I to the conditions of a standard drum, it appears that acids containing 1 percent fluoride could be stored at 170° F for periods of at least 2 years without appreciable corrosion or contamination of the acid by corrosion products.

SUMMARY OF RESULTS

A quantitative investigation of the effect of fluoride on the corrosion of 2S-0 aluminum and 347 stainless steel at 170° F by fuming nitric acid was conducted. The results of this investigation can be summarized as follows:

(1) For acid containing no fluoride, the loss in weight of aluminum due to corrosion is approximately $1/5$ that of stainless steel.

(2) The addition of 1 percent fluoride to the acids reduced the weight loss of both 2S-0 aluminum and 347 stainless steel to practically zero even after 26 days exposure at 170° F .

(3) The minimum quantity of fluoride in white fuming nitric acid required to inhibit corrosion is approximately 0.25 and 0.5 percent for aluminum and stainless steel, respectively; and 0.5 and 1 percent for aluminum, and stainless steel, respectively, in red fuming nitric acid.

(4) The inhibiting action of fluoride ion was found to be immaterial of its source.

(5) Based on electrode potential measurements, the inhibiting effect of fluoride appears to be that of increasing the resistance to, rather than reducing the driving force of, the corrosion process.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, December 16, 1953

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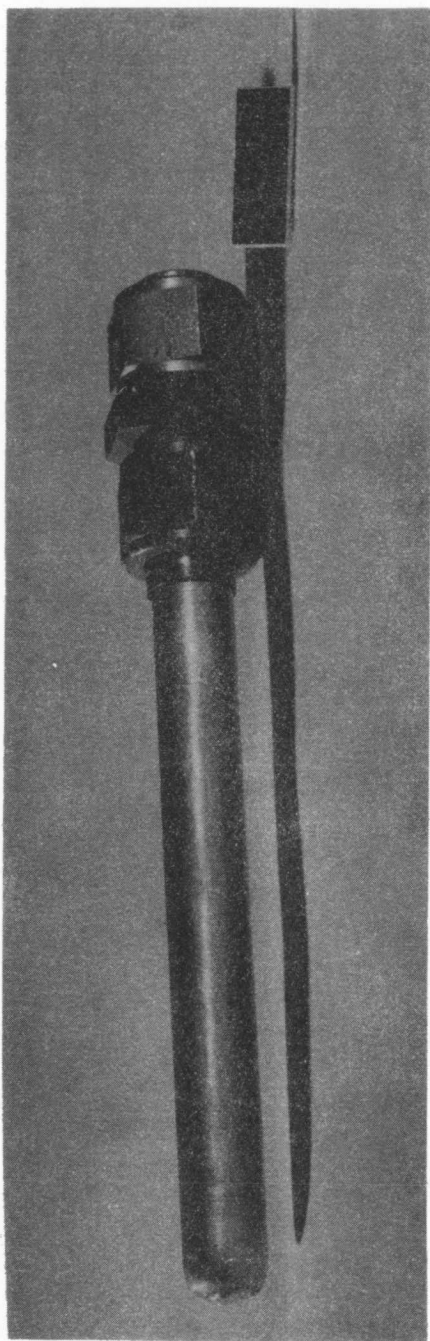
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TABLE I. - WEIGHT LOSS OF SPECIMENS AFTER 26 DAYS EXPOSURE
AT 170° F TO RFNA AND WFNA CONTAINING 1 PERCENT
FLUORIDE (AVERAGE OF TWO RUNS)

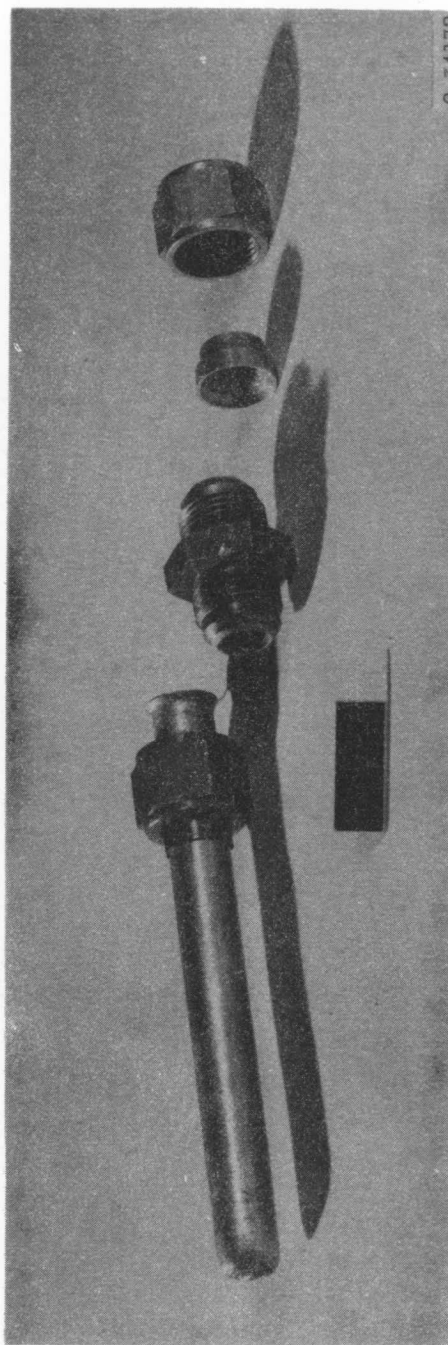
	Weight change, mg			
	Aluminum		Stainless steel	
	RFNA	WFNA	RFNA	WFNA
Before abrasion	9.6	10.6	2.4	1.3
After abrasion	0.2	2.2	-0.2	0.3

TABLE II. - FLUORIDE CONTENT OF RFNA AND WFNA AFTER 26 DAYS AT
170° F IN METAL TEST TUBES (ORIGINAL FLUORIDE
CONCENTRATION, 1 PERCENT)

Acid	Fluoride concentration, percent by wt.	
	Stored in Aluminum	Stored in stainless steel
RFNA	0.38	0.60
WFNA	.31	.42



(a) Assembled .



(b) Disassembled .

Figure 1. - Experimental tube.

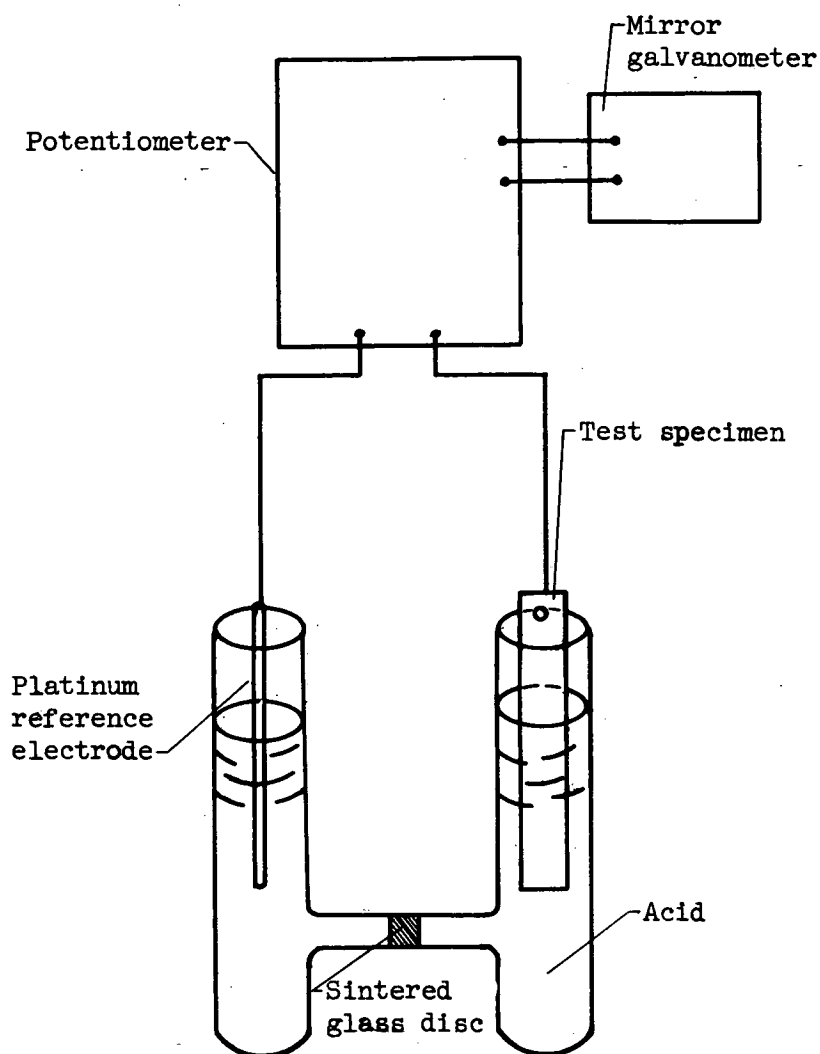
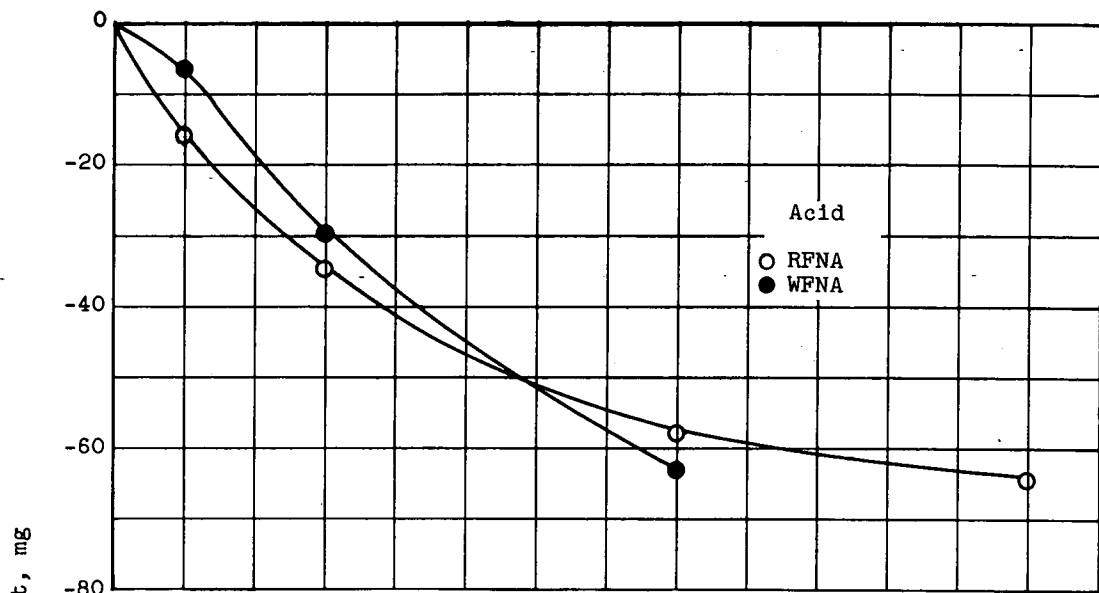
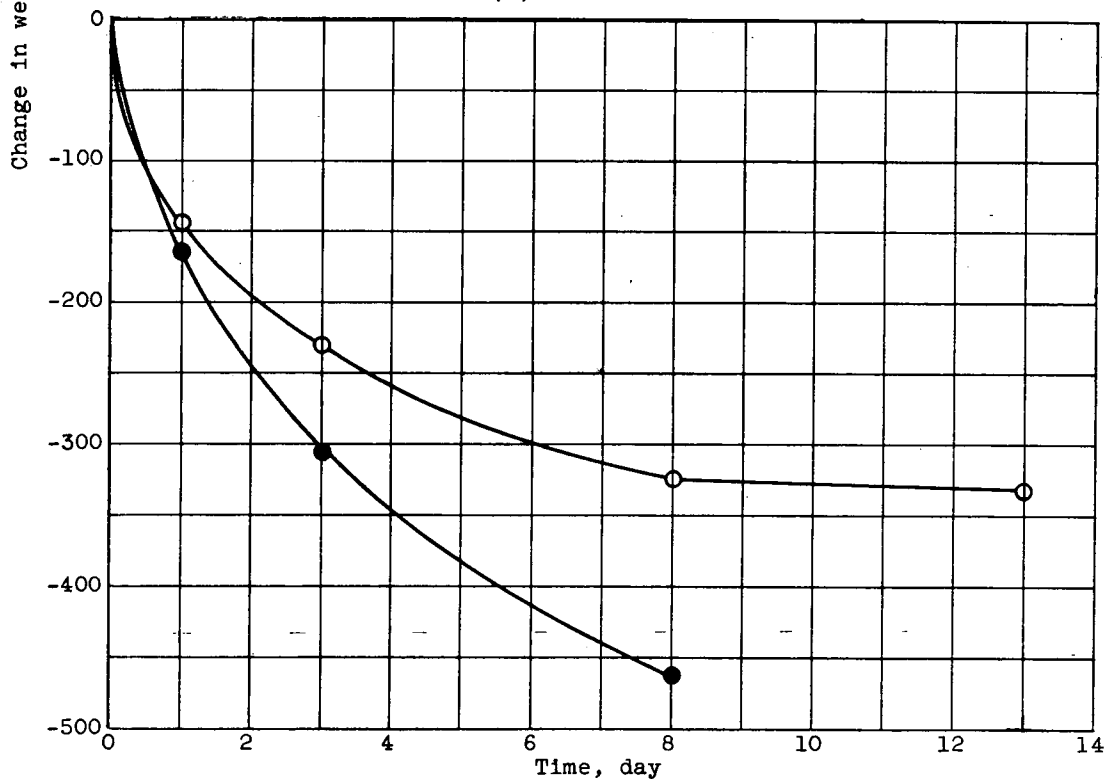


Figure 2. - Electromotive-force cell and instrumentation.

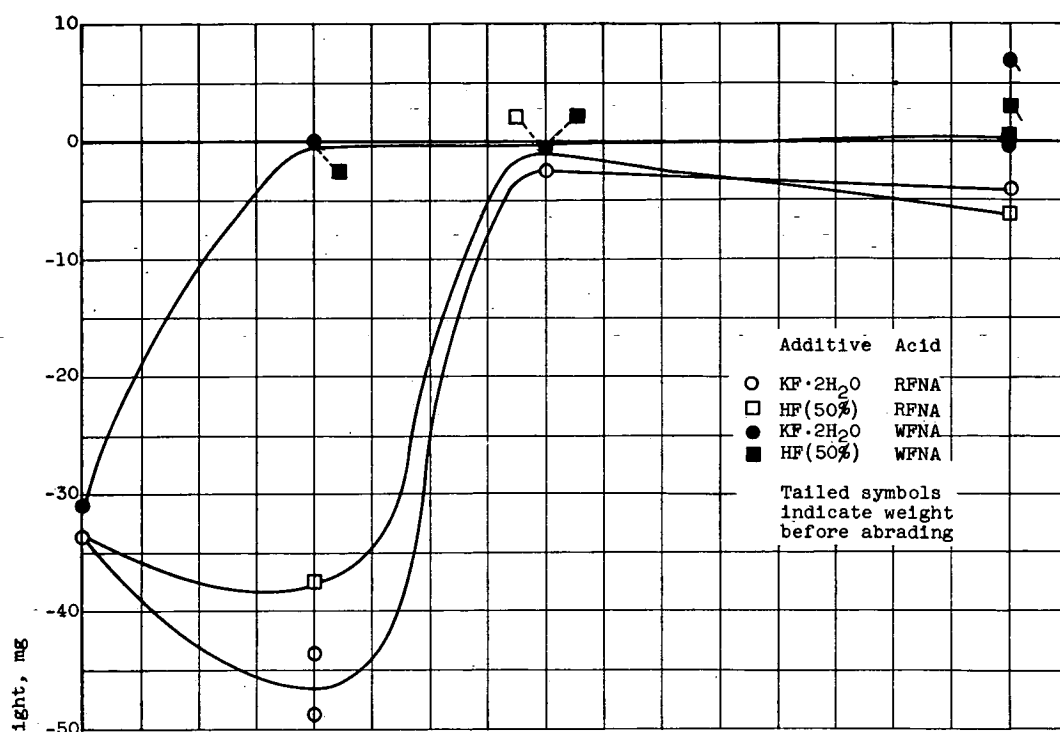


(a) 2S-O Aluminum.

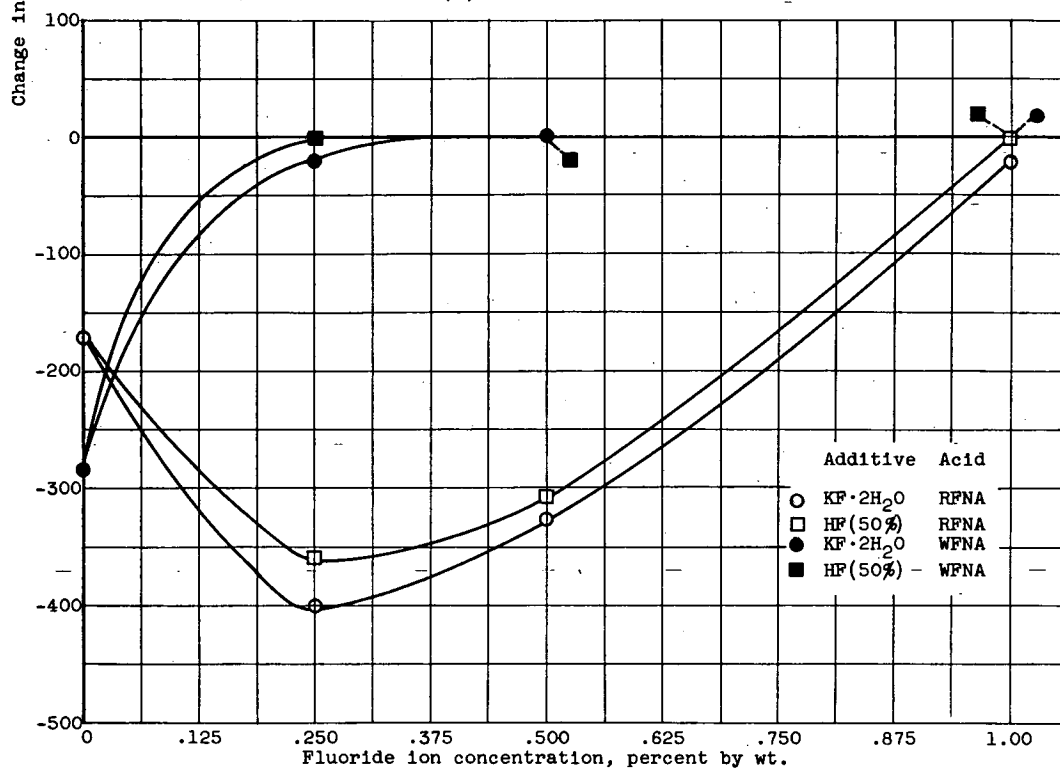


(b) 347 Stainless steel.

Figure 3. - Comparison of weight loss of metal in RFNA and WFNA at 170° F.



(a) 2S-0 Aluminum.



(b) 347 Stainless steel.

Figure 4. - Effect of fluoride ion concentration on weight loss of metal at 170° F; 3-day test.

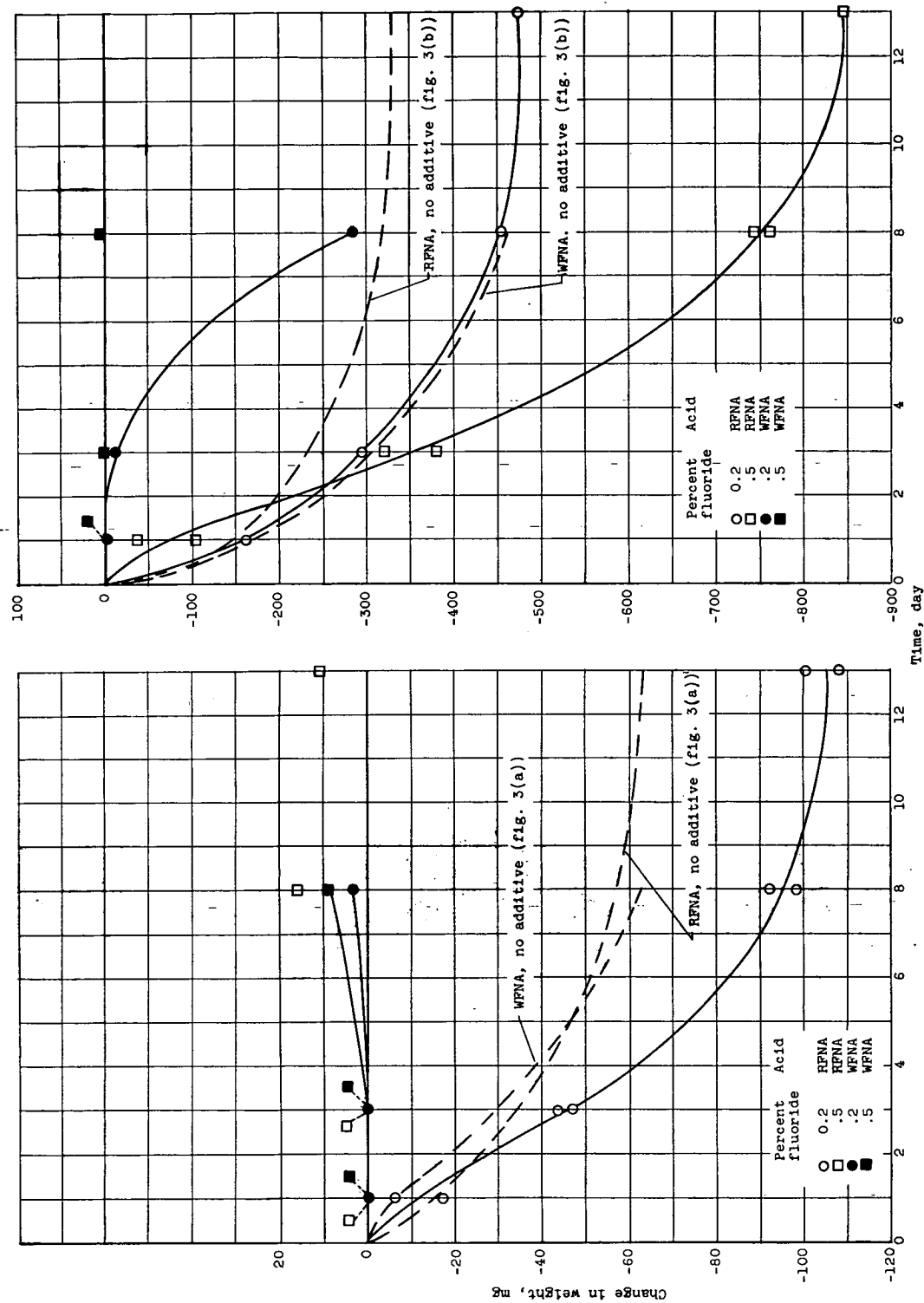
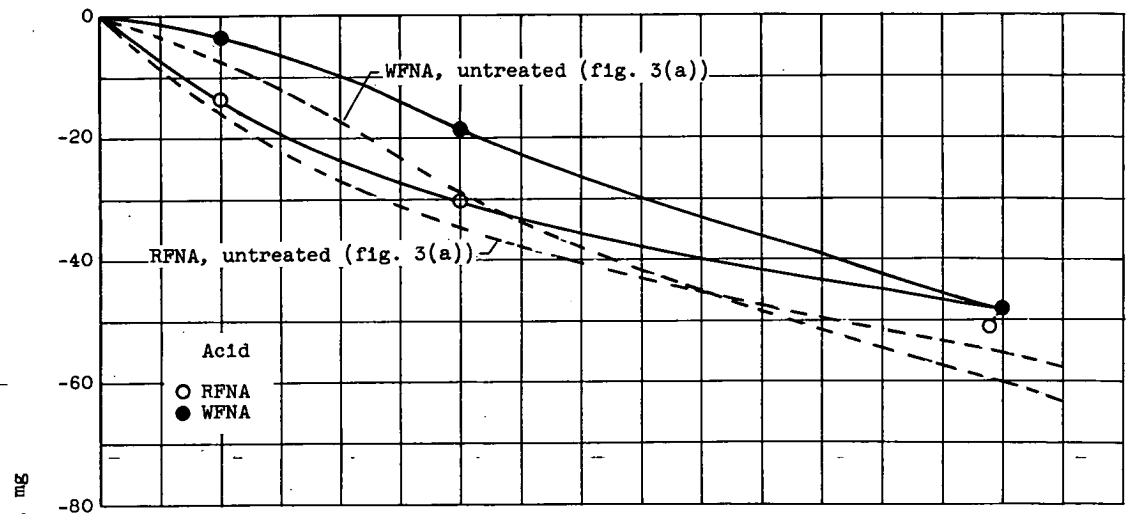
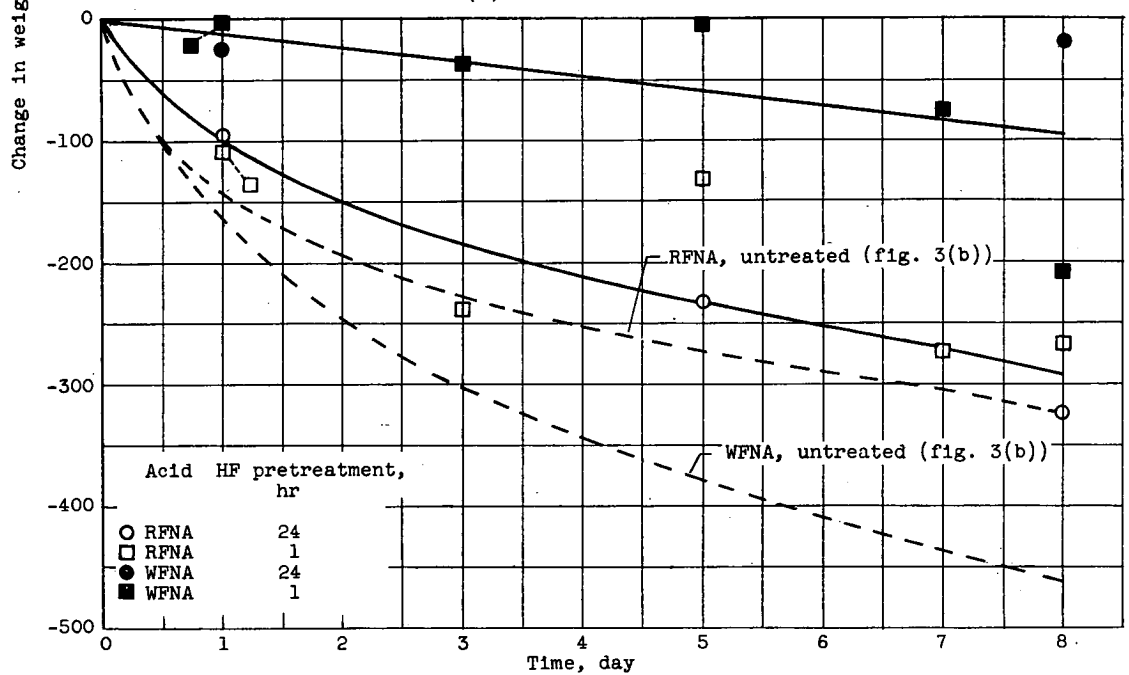


Figure 5. - Effect of time on corrosion of metal in RFNA and WFNA containing 0.2 percent and 0.5 percent fluoride.

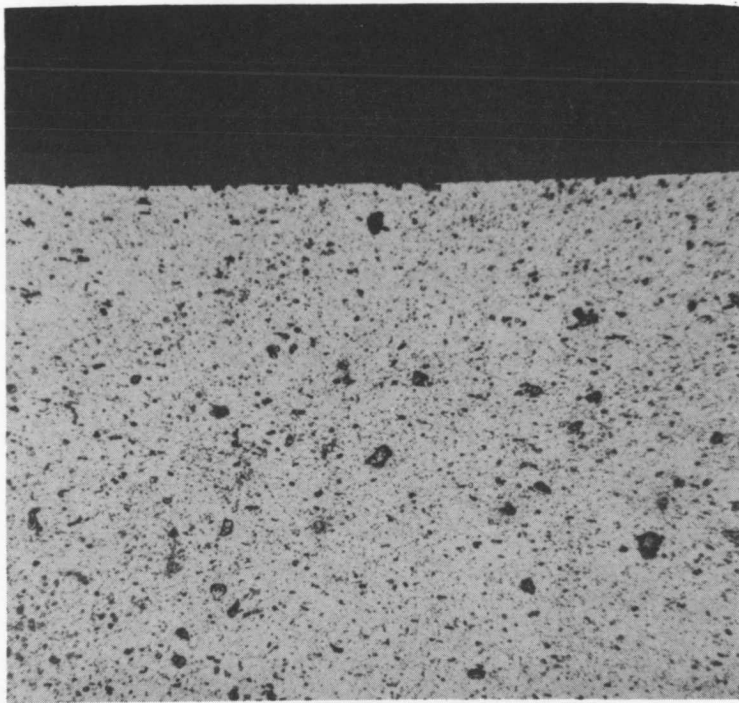


(a) 2S-0 Aluminum.

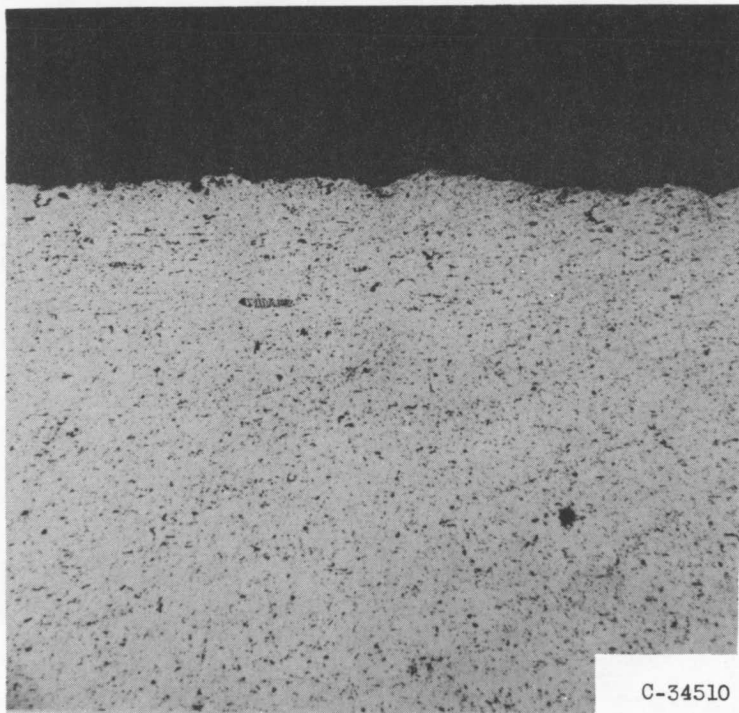


(b) 347 Stainless steel.

Figure 6. - Effect of HF pretreatment on corrosion of metal.



Original specimen

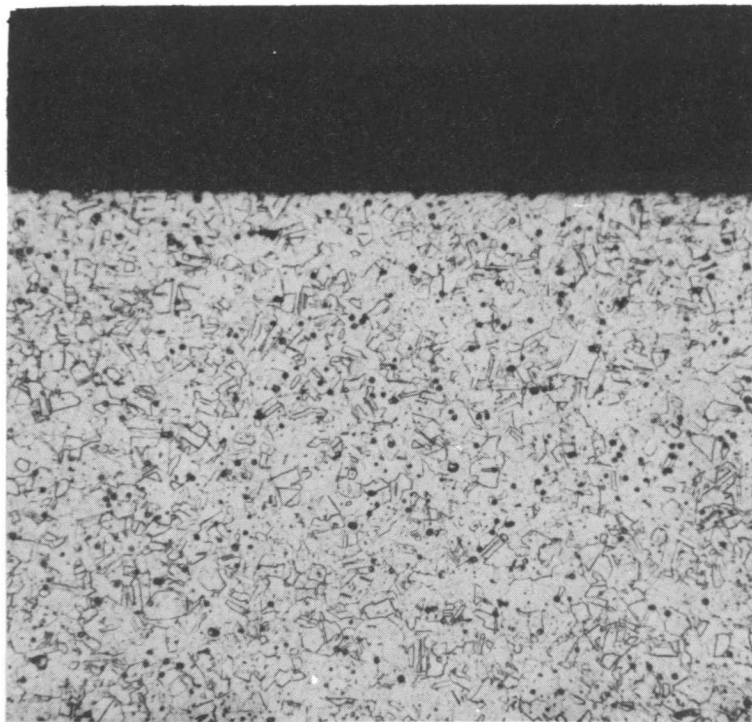


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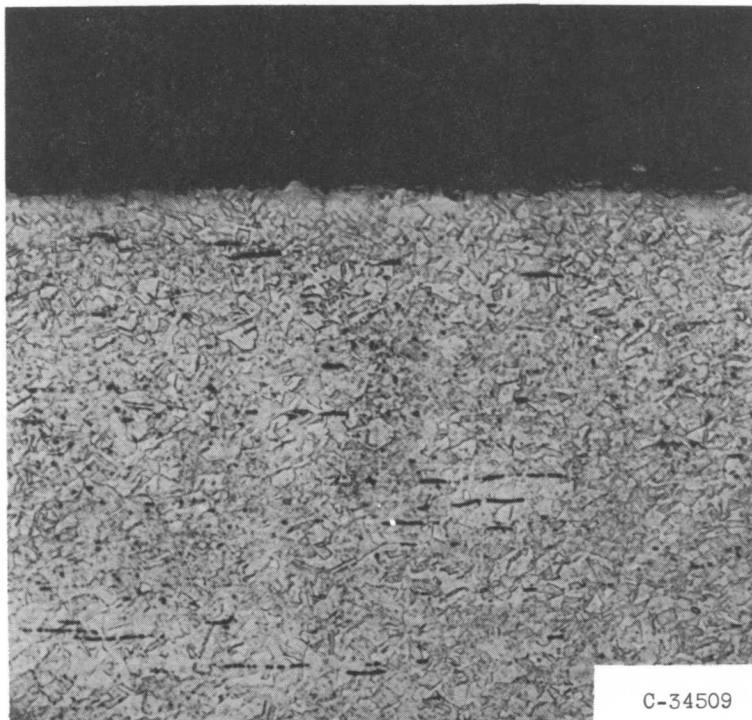
Corroded specimen

(a) Aluminum.

Figure 7. - Photomicrograph of cross sections of metal before and after exposure to RFNA for 13 days. 250X.



Original specimen

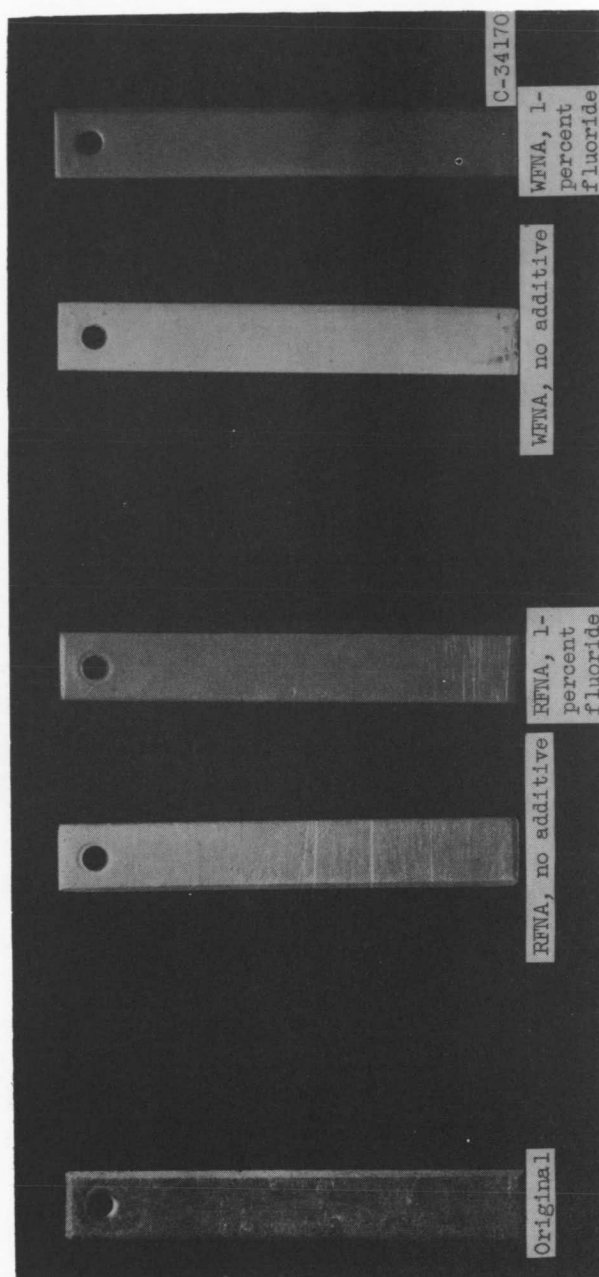


C-34509

Corroded specimen

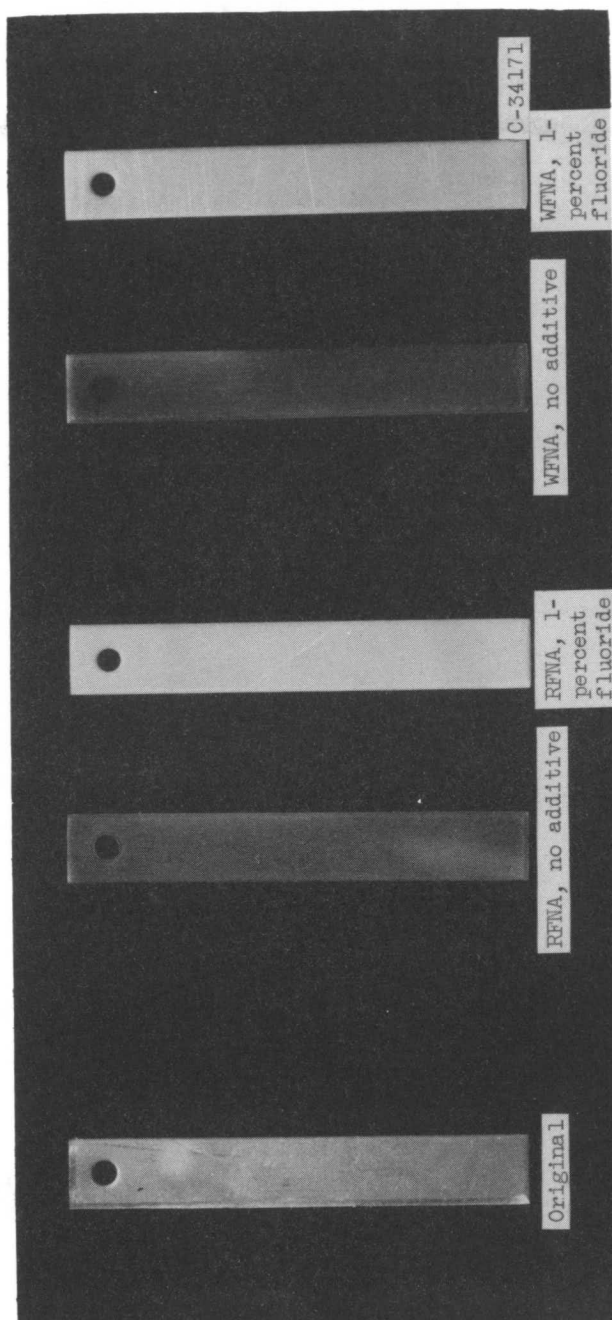
(b) Stainless steel.

Figure 7. - Concluded. Photomicrograph of cross sections of metal before and after exposure to RFNA for 13 days. 250X.



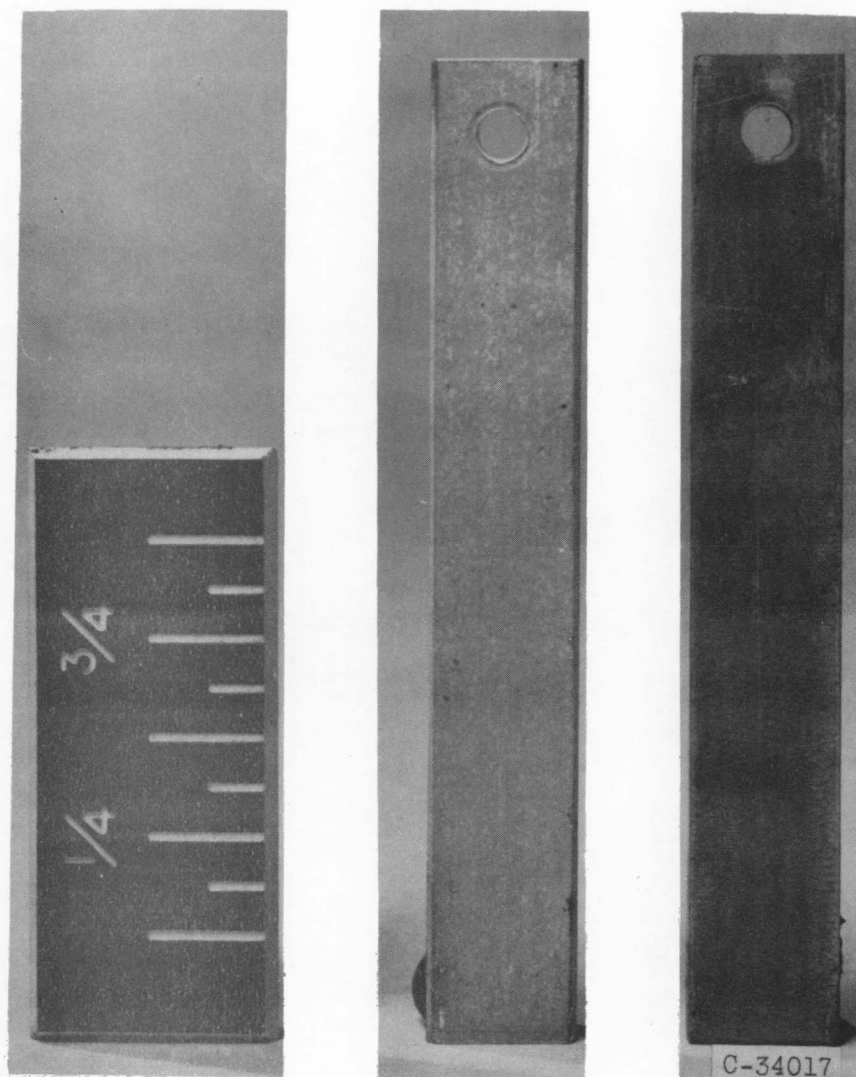
(a) Aluminum.

Figure 8. - Metal specimens before and after exposure at 170° F to WFNA and WFNA with and without 1 percent fluoride for 3 days.



(b) Stainless steel.

Figure 8. - Concluded. Metal specimens before and after exposure at 170° F to WFNA and WFNA with and without 1 percent fluoride for 3 days.



(a) Aluminum.

(b) Stainless steel.

Figure 9. - Aluminum and stainless steel specimens after 10 days of exposure to acid containing 1-percent fluoride.

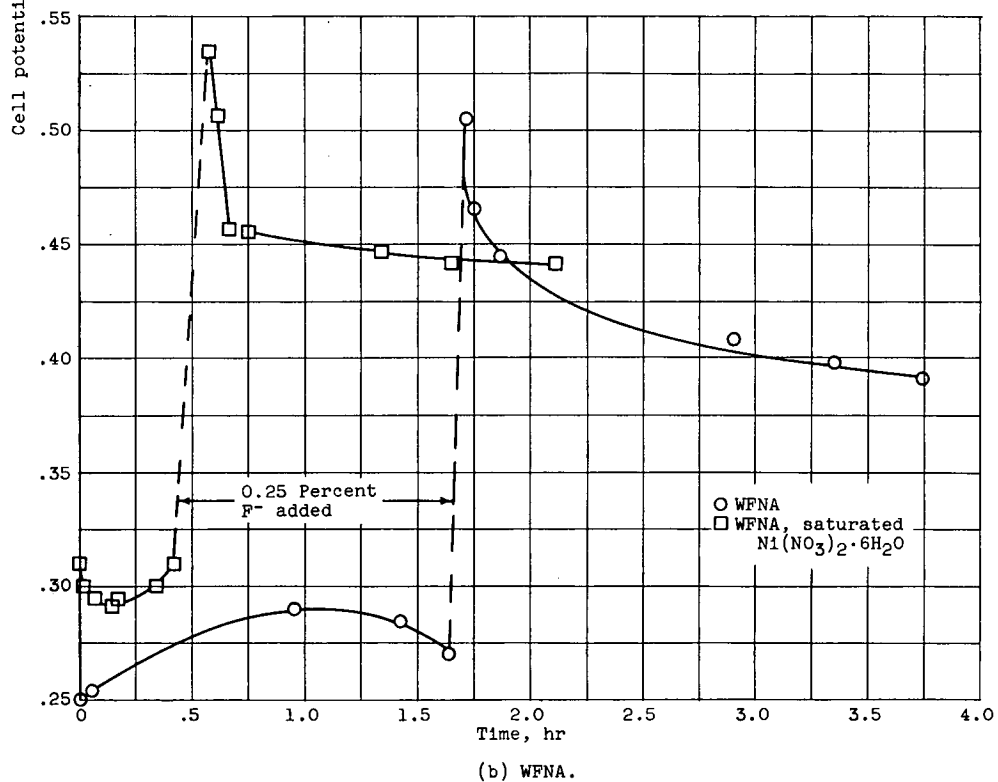
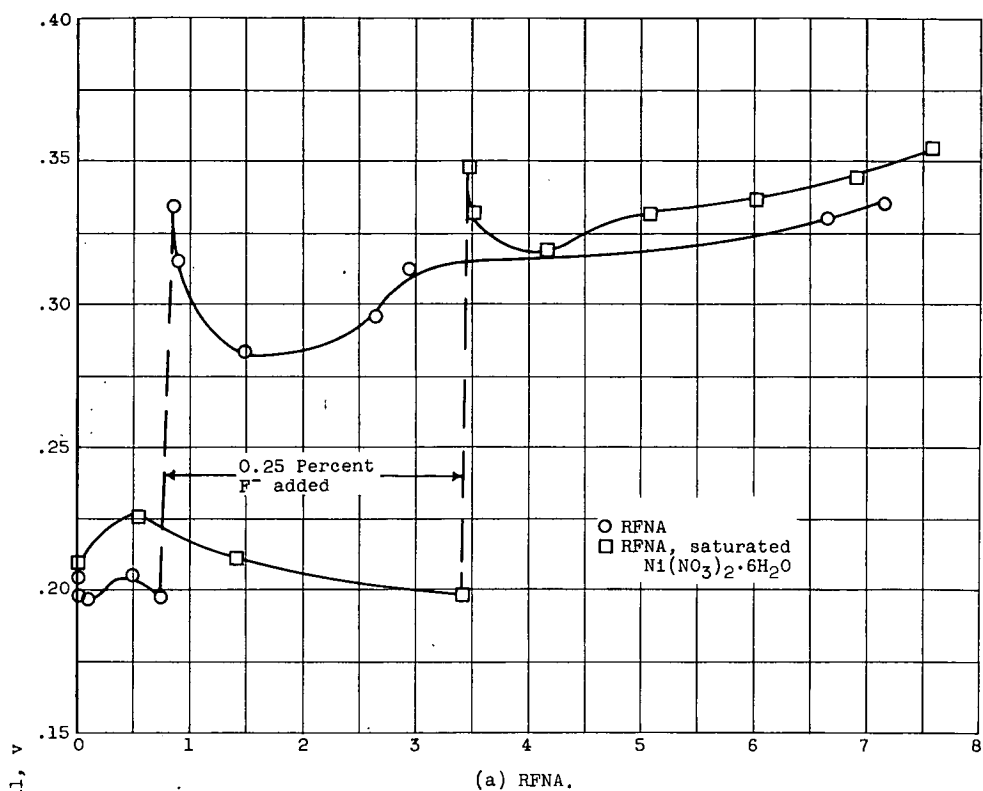


Figure 10. - Effect of fluoride on electrode potential of stainless steel in acid.